Bound by biodegradability

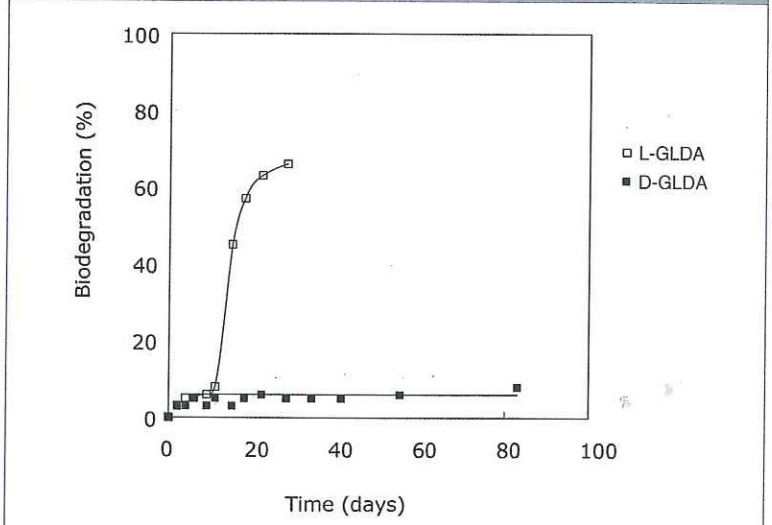
Replacing classic chelating agents with greener materials is a difficult task for the formulator. J Seetz and G P Stafford introduce a new biodegradable chelating agent

The search for a cost effective alternative to the two most frequently used chelating agents NTA (nitrilotriacetic acid) and EDTA (ethylenediaminetetraacetic acid) has long been an industry target. Such an alternative has to possess a good ecological and toxicological profile. Adding a third requirement - that the product should largely be made from renewable sources - gave the R&D work a new dimension.

While developments have largely been driven by the Industrial and Institutional (I&I) formulators' desire for a greener portfolio of raw materials, extra impetus has come from customers of the formulators who have made the decision in the past to restrict the use of EDTA. In fact, contrary to earlier beliefs, biological pathway studies have shown that EDTA is biodegradable in the environment and has a good and well tested toxicological profile. As a consequence, the limited risks to man and his environment are identified and, more importantly, they are also easily managed. However, with the decision to replace EDTA made before this was all known, an alternative is still needed.

There are a number of alternative products on the market which claim to be as effective as EDTA and NTA but most also have their restrictions. Organophosphonates, for example, were found to be not readily biodegradable. Others are readily biodegradable, such as citrates and gluconates, but do not have a sufficiently strong chelating power compared to NTA or EDTA. It has therefore been difficult to find a good solution that matches the performance profile of traditional chelating agents.

Figure 1 - Biodegradation of L-GLDA and D-GLDA in Closed Bottle tests inoculated with activated sludge



To meet stringent green requirements, Akzo Nobel has an ongoing R&D programme for new products and as part of this it has introduced Dissolvine GL, containing GLDA (glutamic acid diacetic acid). GLDA is a direct alternative to NTA and EDTA, fulfilling all of the targets set above.

Dissolvine GL is classified as readily biodegradable (>60% degraded within 28 days) according to the internationally recognised OECD 301D test protocol. The product consists only of L-GLDA. This is significant because the D-form is not biodegradable (see figure 1). This exclusivity for the L form is based on the fact that it is made of a naturally occurring amino acid, L-glutamic acid. This material is food approved and regarded as a safe food additive (US EPA GRAS). It is used in many foodstuffs to improve flavour properties and is a toxicologically sound building block.

From a carbohydrate source such as sugar, molasses, corn or rice, GLDA is produced using a biochemical process to give the pure L-isomer that is required to meet the readily biodegradable profile. The material is later modified using proprietary technology to produce a strong chelating agent. GLDA has been refined and improved, based on experience gained from other chelating agents, to yield a product with excellent sequestering power and solubility.

A large number of toxicity tests reveal that GLDA is not a dangerous chemical (no CMR) and that it has excellent properties with regard to eco and human toxicity. GLDA can be regarded as non hazardous when put into water (NWG according to German Water Endangering Class).

With regard to the green nature of GLDA, the molecule is largely based on natural, replaceable and sustainable raw materials (see figure 2). According to the Bra Miljöval protocol of the Swedish Society for Nature Conservation, it is 86% based on renewable resources, a much higher proportion than other chelating agents.

In trials, GLDA has proved to have an optimal balance between biodegradability, metal chelation and ease of use. Unusual but interesting physical properties include high water solubility over a wide pH range (see figure 3). For example, GLDA is about 2 mole/kg soluble (≈ 50 weight %) in water at a pH of 2.

Figure 2 - GLDA-Na4 fossil & green character

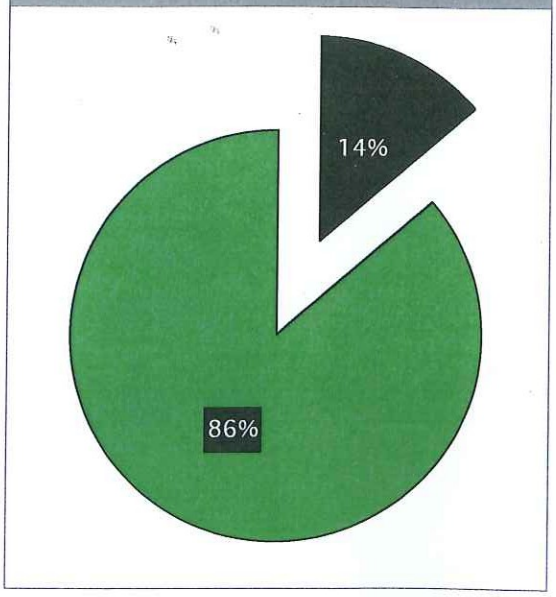


Figure 3 - Solubility of chelating agents in water at various pH levels

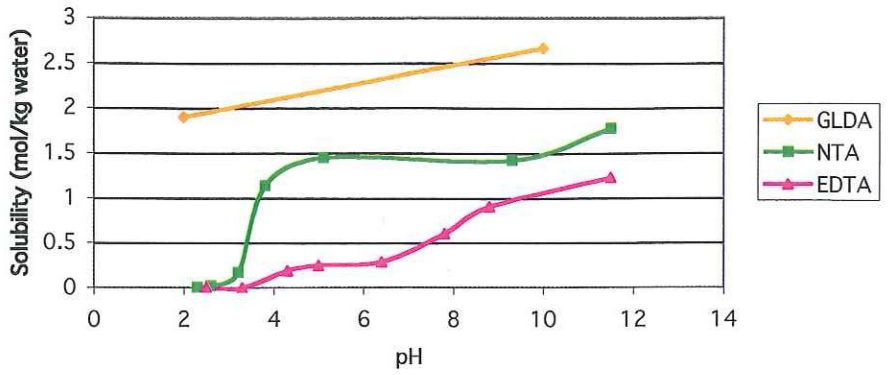
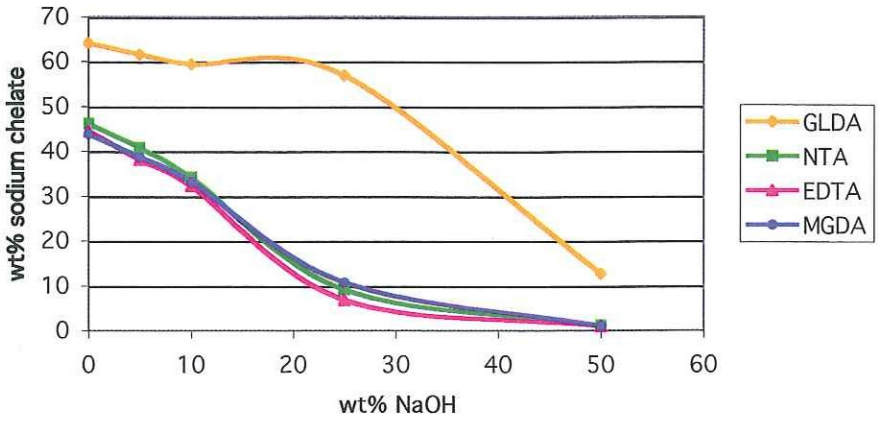


Figure 4 - Solubility of chelating agents in concentrated sodium hydroxide solution



This is high in comparison to classic chelating agents, like EDTA, which have approximately 0.1 weight % solubility under similar conditions. This is significant for cleaning products (such as cleaning in place) that are formulated at low pH.

EDTA and NTA are known to be thermally stable (>150°C). In thermographic experiments GLDA is surprisingly stable. When tested at temperatures >300°C it showed no significant decomposition. This property has been used to develop water treatment systems for operating boilers to reduce the effect of hard water metals and other metals released into the water due to operating conditions; iron for example.

GLDA behaves similarly in cleaning formulations to liquid NTA and EDTA, making their replacement possible without major modifications to the surfactant systems. The benefit of GLDA in such formulations is its broad effective pH range for the chelation of the hard water ions even at very high pH levels (>pH 11). This is significant because it also has a high solubility in sodium hydroxide-based systems. Tests have shown up to ten times higher solubility levels in 25% NaOH solution compared to products like the sodium salts of EDTA and NTA (see figure 4). This creates the opportunity for formulators to work either with more concentrated formulations due to the higher water solubility and/or formulations containing higher levels of sodium hydroxide that are currently restricted due to the solubility of other chelating agents.

GLDA is an excellent alternative to NTA and EDTA in all of the normal industrial cleaning applications. In addition it has further potential uses in the strongly alkaline hard surface cleaning agents used in food processing, kitchen cleaning and automatic dishwashing products.

There is also increased interest in the use of disinfectants in formulations. Like EDTA, GLDA can be used in combination with biocides to improve the biocidal performance of a disinfection system. GLDA is not a biocide but is believed to chelate calcium ions in the bacteria cell walls whereby the bacteria become more sensitive to the active biocides. The use of a biodegradable chelating agent in such a system is novel.

GLDA is also used in personal care and cosmetic products and has the INCI name Tetrasodium glutamate diacetate. It is free from genetically modified raw materials and is not irritating to skin or eyes, properties that are of course particularly attractive in the development of new cosmetic products.

Replacing the classic chelating agents - NTA and EDTA - is a difficult task for the formulator. However, GLDA has proven to be an effective alternative to these products in commercial applications and it distinguishes itself from other potential replacements in its natural amino acid raw material base, its strong chelating power and its unusual physical chemical properties. GLDA enables the formulator to develop products that are cost effective with a brighter, environmentally friendly future.

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